REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION BY ADSORPTION

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USUWANIE BŁĘKITU METYLENOWEGO Z ROZTWORÓW WODNYCH W PROCESIE ADSORPCJI

W artykule przedstawiono wyniki badań laboratoryjnych dotyczących możliwości wykorzystania węgli aktywnych produkcji polskiej oraz niekonwencjonalnych adsorbentów takich jak modyfikowana glinka Clarion i klinoptylolit do usuwania błękitu metylenowego z wody. Celem przeprowadzonych badań było ilościowe sformułowanie procesu adsorpcji oraz ustalenie wpływu różnych czynników na jego przebieg. Nakreślone w celu pracy zadania próbowano rozwiązać posługując się modelowymi układami doświadczalnymi. Jako adsorptyw stosowano roztwór błękitu metylenowego o stężeniu 20 mg/dm³ sporządzony na bazie wody destylowanej. Procesy adsorpcji prowadzone w układzie porcjowym najlepiej opisywały izotermy Freundlicha. Na podstawie izoterm wyliczono zdolność adsorpcyjną testowanych adsorbentów. Warunki przepływowe realizowano metodą filtracji kolumnowej. Na podstawie uzyskanych wyników sporządzono krzywe przebicia – izoplany, które posłużyły do wyznaczenia pojemności adsorpcyjnych w warunkach przepływowych. Użyteczne pojemności adsorpcyjne wyznaczone na podstawie izoplan wynosiły odpowiednio: węgle aktywne 27,00–41,00 mg/g, modyfikowana glinka Clarion 14,68 mg/g, klinoptylolit 5,54 mg/g. Krzywe wyjścia (izoplany) posłużyły do określenia strefy przenikania masy (wysokości frontu adsorpcji) oraz do obliczenia prędkości przesuwania się strefy wymiany masy. Modyfikowana glinka Clarion oraz klinoptylolit pomimo gorszych właściwości adsorpcyjnych mogą być brane pod uwagę jako materiały osłonowe w stosunku do węgli aktywnych.

Summary

The paper presents the results of laboratory tests concerning the possibility of utilizing activated carbons produced in Poland, as well as of non-conventional adsorbents, such as modified Clarion clay and clinoptylolite, for removing methylene blue from water. The objective of tests carried out was a quantitative formulation of the adsorption process, as well as the determination of the effects of various factors on its course. The attempt was taken to solve the tasks defined in the objective of the study using model experimental systems. The methylene blue solution in concentration 20 mg/dm³, prepared on the basis of distilled water, was used as adsorbate. Adsorption processes, conducted in batch mode (in no-flow conditions), were best described by the Freundlich isotherms. On the basis of the isotherms the adsorptive capacity of tested adsorbents was calculated. The through-flow conditions were realized by a columnar filtration method. On the basis of obtained results the breakthrough curves (isoplanes) were plotted. The adsorptive capacities, determined on the basis of isoplanes reached 27–41 mg/g, 14.89 mg/g and 5.54 mg/g for activated carbons, modified Clarion clay and clinoptylolite, respectively. Exit curves (isoplanes) served for defining the mass transfer zone (the adsorption front height), as well as for calculating the mass-exchange-zone moving rate. Despite their inferior adsorptive characteristics the modified Clarion clay and clinoptylolite may be taken into account as shielding materials in relation to activated carbons.

INTRODUCTION

The basic function of the adsorption process is to remove low-concentration diluted organic substances, including those having detrimental effect on the organo-leptic properties of water as well as those toxic and/or carcinogenic for humans. This process is generally one of the last stages in potable-water conditioning. The physical and chemical characteristics of adsorbents strongly affect the course of adsorption process, which, being a surfacial phenomenon is directly proportional to the specific surface of the adsorbents [8].

Activated carbons are commonly known and used adsorbents, but their high price is the reason why the search is continued for other, cheaper but nonetheless effective adsorbents, such as naturally occurring and treated zeolites, clinoptylolite, diatomite, bentonite, kaolin and other smectite clay minerals, mineral-and-carbon materials, carbonizing agents or semi-cokes [2, 4, 9, 12–14].

Correct use of adsorbents in water technology processes requires good understanding of adsorption processes. The adsorptive capacity of applied adsorbents and the effect of various factors on the course of the adsorption process shall be determined in laboratory studies. A general mathematical model describing the adsorption equilibrium does not exist due to the large variety of adsorbent – adsorbate system. However, there are many empirical and semiempirical equations describing the course of the adsorption isotherms. The adsorption isotherm equations that are commonly used to describe the experimental adsorption data are those developed by Freundlich, Langmuir and BET [1, 5, 6, 11].

The methylene blue is the substance which is frequently used in testing of adsorbents to represent organic compounds [2, 7, 10].

MATERIALS AND METHODS

Sorption materials used for testing
Modified clay Clarion
Clarion is a sorbent produced by the CETECO Wastewater Group. It is a mixture of clay (30% by weight) and anthracite (70% by weight). It has a lamellar structure. Through suitable processing the clay structure becomes modified with amines to make it as hydrophobic as possible with a low affinity for water and a high affinity for organic substances. The grain size of the adsorbent used was between 0.4 and 1.2 mm.

Clinoptylolite
Clinoptylolites are aluminosilicates with a skeleton structure, containing free spaces filled with large ions and water molecules. Silica content varies in the range of 54.4–66.6%, and alumina content is in the range of 13.2–18.35%. Clinoptylolites may occur in sedimentary (argillaceous schist-clay shale), volcanic (tuffs), and in metamorphic rock. In Poland, strata of this mineral occur mainly in sedimentary rocks where the content of pure clinoptylolite in mudstone ranges from 4% to 30%. The content of pure clinoptylolite in tuffs is quite considerable and varies in the range of 60–90%. Rich deposits of tuffs are located in Slovakia and Ukraine. Clinoptylolites used for this research are from Slovakia (near Koszyce). The initial treatment of clinoptylolite consisted in isolation (through sieving method) of the 0.75–1.2 mm fraction (typical grain size used in waste-water treatment processes), washing, drying at 105°C.

Activated carbons

Activated carbons WD-extra, WG-15 and AG-5 produced in Poland were used for comparative study. They had a grain size of 1.0–1.5 mm, with a grain-size distribution unevenness (uniformity) coefficient – 1.2; a total volume of pores was 0.85–0.95 cm^3/g, and a specific surface (Brunauer – Emmett – Teller (BET) method, N_2) varying from 950 to 1050 m^2/g (Tab. 1).

Table 1. Characteristic of activated carbons

Designation	Unit	WD-extra	WG-12	AG-5
Specific surface area (BET,N_2)	m^2/g	950–1050	1250	950–1050
Iodine number	mg/g	900–1000	1160	900–1000
Methylene number	cm^3	min. 22	35	min. 25
Granulation	mm	1.0–1.5		0.75–1.2
Coefficient of grain-size distribution unevenness		1.2		1.2
Total volume of pores	cm^3/g	0.85–0.95		0.8–0.9
Adsorption of phenol	%	4–5	4	

Methods

The model experiment system consisted of the following adsorbents: Clarion modified clay, clinoptylolite and activated carbons. Solutions of methylene blue of concentration 20 mg/dm^3, prepared on distilled water basis, were used as adsorbates.

The concentration of methylene blue was determined by colorimetric analysis referred to a scale of specific standards.

Adsorption kinetics was determined for Clarion clay and clinoptylolite at a dose of 10 g/dm^3 and activated carbons at a dose of 1 g/dm^3. A suitable adsorbent was added to a number of conical flasks each containing 300 cm^3 of model solution and shaken (at 150 r.p.m.) for 10, 20, 30, 40, 50, 60, 80, 100, 120 and 180 minutes. Testing was conducted with pH oscillating around neutral (pH = 7.0). The clarification time was one hour. These parameters were optimized in preliminary technological research. The control determination was carried out in decanted solutions.

The effect of pH of adsorptive solutions on the adsorption process was studied with the use of sorbents and their doses such as those for the determination of adsorption kinetics. The pH value of model solutions was varied within 5–10. The shaking time was 30 minutes and the decanting time – 1 hour.

In order to determine the adsorption isotherms, increasing doses (3–30 g/dm^3 of Clarion clay and clinoptylolite and 0.3–3.0 g/dm^3 of activated carbons) were added to eight conical flasks containing each 300 cm^3 of model solutions. Sample temperature was stabilized at 15°C, and the samples were shaken for 30 minutes in insulation. Then they were left for one hour and methylene blue was determined in the decanted solution.

Dynamic conditions were realized (defined) by the column filtration method. The adsorption columns were made of organic glass of diameter 32 mm. The filling height was 750 mm and the adsorbent quantities in the column were: 0.470 kg for Clarion clay,

0.650 kg for clinoptylolite, and 0.313–0.322 kg for activated carbons. Filtration was performed from the top downwards. At the beginning of each filtration cycle the filtration rates were changed consecutively to 6, 8, 12, 18 and 20 m/h, while the optimum rate was determined. Further testing in a given cycle was performed at filtration rates of 12 m/h for Clarion clay and clinoptylolite, and 20 m/h for activated carbons. After each hour of bed operation, samples were taken in order to carry out control analyses. Filtration lasted each time until the moment of bed exhaustion, i.e., at the point where the concentration in the discharge becomes equal to that of the initial solution.

RESULTS AND DISCUSSION

As indicated in Figure 1, data on adsorption kinetics showed that the process took place quite rapidly. A complete sorption balance became established after about 2 hours, but the process proceeded with great intensity for 20–30 minutes. In further testing, the shaking time of 30 minutes was accepted as the optimum. It is the time after which the reduction of methylene blue impurities (compounds) was only minimal.
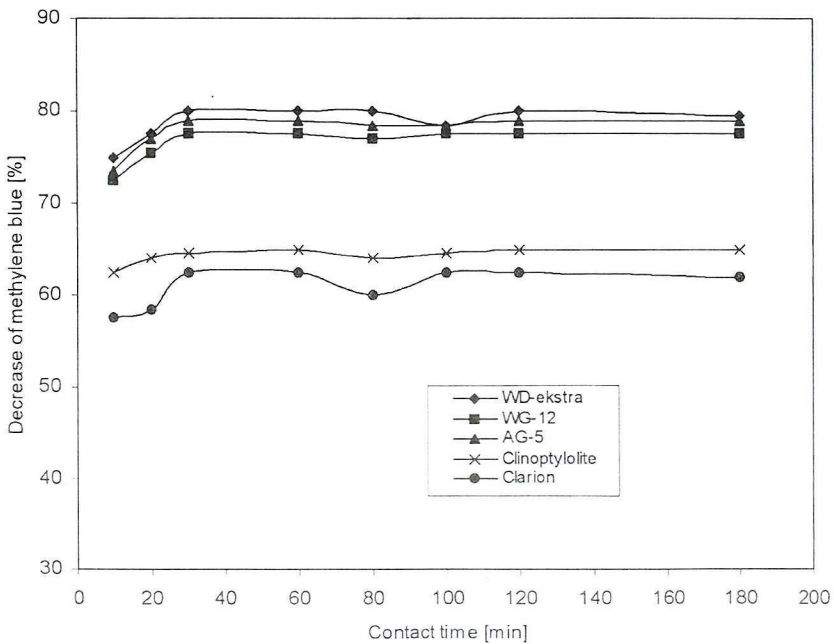

Fig. 1. Effect of contact time on adsorption process

As shown in Table 2, the pH value of adsorbates had a strong effect on the adsorption process. Adsorption of methylene blue impurities proceeded best at reaction lower than 7.0. Much worse results were obtained at pH 9.0–10.0.

Further testing was conducted with pH oscillating around neutral (pH = 7.0), for which good, or even, mostly, best results were obtained.

The results obtained in a successive series of experiments performed in static conditions were described with basic equations of isotherms, i.e., those of Freundlich, Langmuir and BET. Langmuir's and BET isotherms exhibited low matching to empirical values (coefficients of correlation ranged within 0.50–0.70). The adsorption processes were best described by Freundlich's isotherms. Their choice was dictated by a high correlation coefficient, R approx. equal to 0.9 (Tab. 3).

The Freundlich isotherms were determined in linear form, approximated with the least-squares method, described with mathematic equations and isotherm constants, n and K, were determined on their basis (Tab. 3).

Analyzing the course of isotherms (Fig. 2) it was found that activated carbons exceeded the rest of adsorbents in respect of adsorption ability. Values of capacity adsorption were compiled in Table 4.
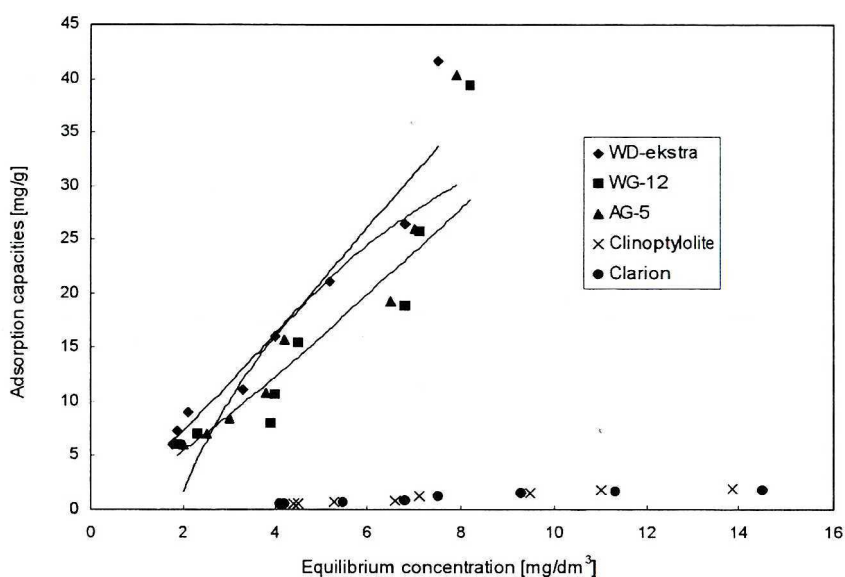

Fig. 2. Adsorption isotherms

Table 2. Effect of pH adsorbate solutions the effectiveness of the adsorption process

Value of pH of adsorbate solution	Concentration of methylene blue [mg/dm³]				
	WD-extra (dose 1 g/dm³)	WG-12 (dose 1 g/dm³)	AG-1 (dose 1 g/dm³)	Clinoptylolite (dose 10 g/dm³)	Clarion (dose 10 g/dm³)
5.0	4.6	4.6	4.4	7.2	7.5
6.0	4.4	4.6	4.3	7.2	7.6
7.0	4.0	4.5	4.2	7.1	7.5
8.0	4.4	4.9	4.3	7.3	7.8
9.0	4.5	5.1	4.4	7.5	7.7
10.0	4.4	5.1	4.5	7.6	7.6

Table 3. Constants of Freundlich adsorption isotherms

Adsorbent type	Constant of isotherms		Correlation coefficient R
	K	n	
Clarion	0.1347	0.9699	0.97
Clinoptylolite	0.0922	0.8052	0.96
WD-extra	3.2726	0.8643	0.96
WG-12	2.3982	0.8477	0.88
AG-5	2.1933	0.7745	0.94

The adsorptive capacity was calculated, based on determined isotherms (Fig. 2 and Tab. 3).

As shown in Figure 3, the breakthrough curves (isoplanes) were plotted basing on results obtained from column filtration tests.
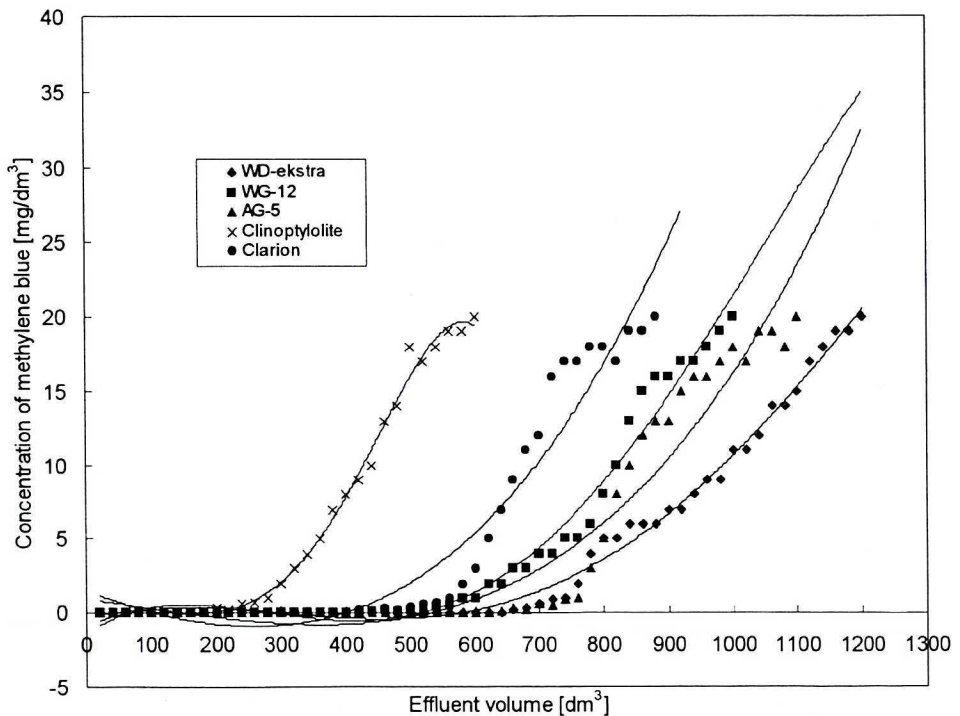

Fig. 3. Adsorption breakthrough curves (isoplanes)

These isoplanes served for the determination of sorption capacities under dynamic conditions (Tab. 4).

Calculations were performed to determine the total adsorptive capacity (until the bed exhaustion point) and usable adsorptive capacity (until the bed breakthrough point) using the filtration curves (isoplanes) plotted during the process and described by means of mathematic equations (1), (2), (3), (4) and (5):

modified clay Clarion $y = 3E-08x^3 + 2E-05x^2 - 0.0168x + 1.4788$ (1)

correlation coefficient R = 0.9418;

clinoptylolite $y = -2E-12x^6 + 2E-09x^4 - 3E-08x^3 - 9E-05x^2 + 0.0119x - 0.3144$ (2)

correlation coefficient R = 0.9951;

activated carbon WD-extra $y = -E-11x^4 + 1E-07x^3 - 7E-05x^2 + 0.0163x - 0.8169$ (3)

correlation coefficient R = 0.9925;

activated carbon WG-12 $y = -8E-11x^4 + 2E-07x^3 - 0.0001x^2 + 0.0298x - 1.4108$ (4)

correlation coefficient R = 0.9798;

activated carbon AG-5 $y = 3E-08x^3 - 7E-06x^2 - 0.0058x + 0.9016$ (5)

correlation coefficient R = 0.9365.

The calculations were carried out in accordance with the diagram presented in Figure 4.
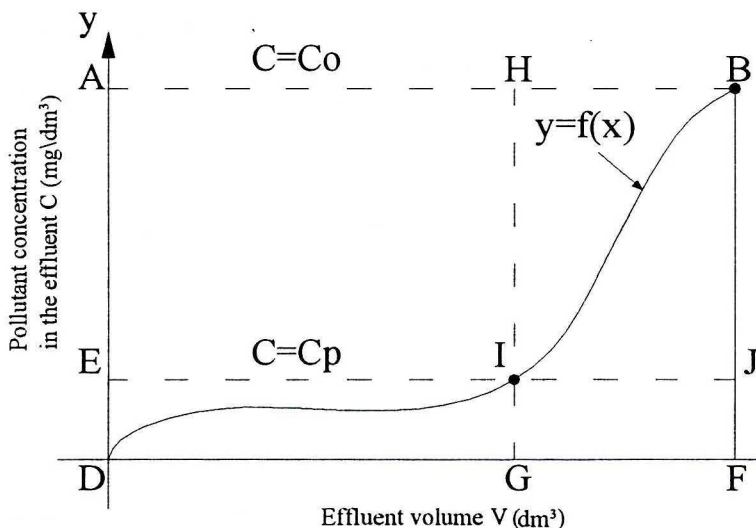

Fig. 4. Supporting drawing for calculation of total and usable adsorptive capacity
C = Co – point of bed exhaustion
C = Cp – breakthrough point

Total adsorptive capacity PAc [g/kg], of specific material was calculated from the following formula, eq. (6):

$$PAc = Oc : M \tag{6}$$

where M is the mass of bed prior to filtration process [g]. The total amount of methylene blue retained in the column, Oc, was calculated from the formula (7):

$$Oc = P_{DFBA} - P_{DFB} = P_{DFBA} - \int_{D}^{F} f(x) \tag{7}$$

where P_{DFBA} is the area representing the quantity of compounds introduced to filtration system (the point of bed exhaustion, $C = C_o = 20$ mg/dm³), P_{DFB} is the area representing the quantity of compounds not retained on the bed (the point of bed exhaustion, $C = C_o$).

The usable adsorptive capacity PAu [g/kg], was calculated as follows, eq. (8):

$$PAu = Ou : M \; [g/kg] \tag{8}$$

The amount of methylene blue retained in the column to the break-through point (Ou), was calculated from the formula (9):

$$Ou = P_{DGHA} - P_{DGI} = P_{DGHA} - \int_{D}^{G} f(x) \tag{9}$$

where P_{DGHA} is the area representing the quantity of compounds introduced to the filtration system (the breakthrough point, $C = C_p = 0$ mg/dm³), P_{DGI} – area representing the quantity of compounds not retained on the bed (the breakthrough point, $C = C_p = 0$ mg/dm³).

The useful capacities of tested adsorbents constituted from 54% (clinopylolite) to 66% (WD-extra) of the total adsorption capacity. In the case of clinoptylolite and Clarion clay the respective values were relatively low.

The isoplanes, determined in tests conducted in flow conditions, also called the exit curves, served for defining the mass transfer zone, which was calculated using the equation of Michaels and Treybal [10]:

$$Ho = H \frac{tw-tp}{tw-(1-\varphi)(tw-tp)} \tag{10}$$

where: Ho – the adsorption front height [cm],
$\quad$ H – the adsorbent bed height [cm],
$\quad$ tw – bed operation time until exhausted [min],
$\quad$ tp – bed operation time until breakthrough [min],
$\quad$ φ – coefficient of sphericity of exit curves was calculated by dividing the surface area of the rectangle HBIJ - $\int_{G}^{F} f(x)$ dx by the surface area of the rectangle HBIJ (Fig. 4, Tab. 5).

Mass exchange zone moving rate, u [cm/min], was calculated from the formula [11] (Tab. 5):

$$u = H_o/(tw - tp) \tag{11}$$

Table 5. The heights of adsorption fronts and the mass exchange moving rates

Adsorbent type	Coefficient of sphericity of exit curves, φ	Heights of adsorption fronts, Ho [cm]	Mass exchange moving rates, u [cm/min]
Clarion	0.512	55,75	0.019
Clinoptylolite	0.593	73.41	0.025
WD-extra	0.721	38.59	0.022
WG-12	0.628	53.05	0.028
AG-5	0.591	37.84	0.018

Materials having lower heights of mass exchange fronts, Ho, and lower rates of their moving across bed heights, exhibit the best adsorptive properties.

Having in mind the above parameters, as well as the values adsorption capacities determined in both non-flow and flow conditions, the tested adsorbents may be ordered as follows:

WD-extra > AG-5 > WG-12 > clinoptylolite > Clarion.

CONCLUSIONS

–   The adsorptive equilibrium between adsorbate solutions and the adsorbents established itself within 2 hours, but the adsorption process was most intensive during the first 20–30 minutes.

–   The pH value of adsorbates had a strong effect on the adsorption process. Adsorption of methylene blue impurities proceeded best at reaction lower than 7.0. Much worse results were obtained at pH 9.0–10.0.

–   The Freundlich isotherm served best for describing the adsorption process. The analysis of isothermal constants leads to a conclusion that activated carbon is the best adsorbent of methylene blue. The Clarion clay may be ranked as the second best, followed by clinoptylolite. The adsorptive capacities determined in static conditions ranked in the same order.

–   The sorption characteristics of studied adsorbents were determined on the basis of the sorption effectiveness and sorption capacity while expressing the mass (in mg) of the pollutant removal by 1 g of sorbent. In respect of adsorption capacities the activated carbons were superior to Clarion clay 2.8 times. The superiority of activated carbons was considerably higher in relation to clinoptylolite as it was 7.2 times.

–   Despite this considerable superiority of activated carbons as sorbent, the modified clay Clarion and clinoptylolite may be taken into account in designing of process systems, especially as shielding materials in relation to activated carbons.

–   The agreement of almost all empirical data from static tests with Freundlich's equation indicates the physical character of the studied phenomena.

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